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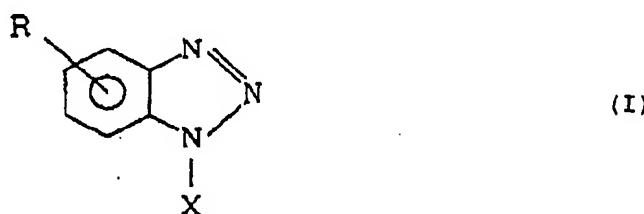
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(54) Recording medium and aqueous ink composition

(57) A recording medium having an ink receiving layer comprising a porous pigment and a binder, wherein the ink receiving layer contains at least one benzotriazole compound represented by formula (I):



wherein R represents a hydrogen atom or an alkyl group; X represents a hydrogen atom, a sodium atom, a potassium atom or a primary, secondary or tertiary amino group. Also disclosed is an aqueous ink composition containing a compound of formula (I) and an ink jet recording method using the recording medium or the aqueous ink composition.

Description**FIELD OF THE INVENTION**

5 [0001] This invention relates to a recording medium and an aqueous ink composition which each provide an image excellent in light fastness and gas fastness and preservable for an extended period of time and, more particularly, to a recording medium and an aqueous ink composition suitable to ink jet recording.

BACKGROUND OF THE INVENTION

10 [0002] With the recent innovative development in ink jet recording technology, the quality of images output on a recording medium by ink jet recording has been increasing, easily standing comparison with silver salt photographic images. However, dyes, which are colorants used to form high-quality images on a recording medium, are susceptible to deterioration by light, such as ultraviolet light and visible light, and oxidizing gases, such as ozone, NO_x , SO_x , H_2S , etc. That is, they have poor light fastness and gas fastness. Therefore, the image recorded in ink comprising a dye as a colorant (hereinafter referred to as dye ink) exhibits, of necessity, poor fastness to light and gas and undergoes discoloration (color change and fading) with time even when kept from intense light, for example, when preserved indoors, still more when exposed to intense light. In other words, the image has poor indoor preservability and is inferior in this respect to silver salt photographs.

15 [0003] On the other hand, recording media for ink jet recording include a so-called swelling type which has an ink receiving layer mainly comprising a polymer, such as polyvinyl alcohol, and a so-called void type (also called absorbing type) which has an ink receiving layer mainly comprising fine porous particles of a pigment, such as amorphous silica, and a binder. These two types differ in degree of deterioration of the dye caught in the ink receiving layer. When an image is recorded on a swelling type recording medium by ink jet recording using dye ink, the dye is buried in the 20 polymer of the ink receiving layer so that it undergoes little discoloration due to air-mediated deterioration, for example, discoloration by air oxidation and air-mediated photodeterioration (generation of singlet state oxygen and resultant decomposition of a dye). On the other hand, when a void type recording medium is recorded by ink jet recording in dye ink, the ink receiving layer, which has a vast number of pores, allows the dye to come into contact with air. It follows that the dye is susceptible to air-mediated deterioration and apt to undergo discoloration. Hence, the problem of air-mediated deterioration of dyes is inherent to void type recording media.

25 [0004] It is known that preservability (indoor preservability) of an ink image formed on a recording medium can be improved by incorporating a benzotriazole ultraviolet (UV) absorber into the ink or the recording medium. However, a benzotriazole UV absorber should be added in a large quantity to manifest a sufficient effect. Besides, addition of a benzotriazole UV absorber to a recording medium tinges the recording medium with yellow and is therefore impractical.

30 [0005] JP-A-9-1922 proposes incorporating a benzotriazole compound different from the above-described benzotriazole UV absorbers into an ink receiving layer. This method aims to present a solution to the problem, which is specific to a swelling type recording medium having an ink receiving layer containing gelatin as a main component, that the image is liable to get uneven in density to have reduced resolving power when allowed to stand open for a long time. There has been made no proposals as to a method for preventing air-mediated dye deterioration which occurs specifically to a void type recording medium thereby to provide an image with improved preservability.

SUMMARY OF THE INVENTION

35 [0006] An object of the present invention is to provide a recording medium and an aqueous recording ink composition capable of providing an image which exhibits excellent fastness to light and gas and is prevented from air-mediated dye deterioration specific to a void type recording medium, particularly capable of providing an image which can be preserved indoors for an extended period of time without substantial discoloration.

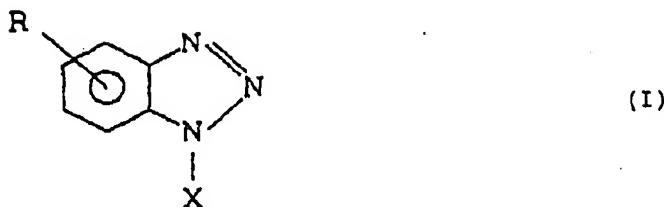
[0007] Other objects and effects of the present invention will become apparent from the following description.

40 [0008] As a result of extensive investigation, the inventors of the present invention found that air-mediated dye deterioration inherent to a void type recording medium can be prevented to improve indoor image preservability (i.e., light fastness and gas fastness) by incorporating a benzotriazole compound having a specific structure into an ink receiving layer of a recording medium and/or a dye ink composition used for recording.

[0009] The present invention is based on this finding.

45 [0010] That is, the above-described objects of the present invention have been achieved by providing the following recording media, aqueous ink compositions, and ink jet recording methods.

- 1) A recording medium having an ink receiving layer comprising a porous pigment and a binder, wherein said ink receiving layer contains at least one benzotriazole compound represented by formula (I) :



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wherein R represents a hydrogen atom or an alkyl group; X represents a hydrogen atom, a sodium atom, a potassium atom or a primary, secondary or tertiary amino group.

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2) The recording medium according to item 1) above, wherein said benzotriazole compound comprises at least one of benzotriazole, benzotriazole sodium salt, 4-methylbenzotriazole, 4-methylbenzotriazole sodium salt, and a benzotriazole amine salt.

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3) The recording medium according to item 1) or 2) above, wherein said benzotriazole compound is present in a total amount of 0.01 to 5% by weight based on the weight of said ink receiving layer.

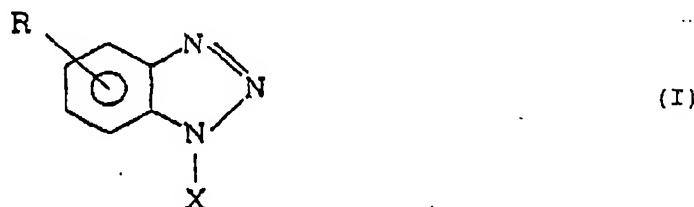
4) The recording medium according to any one of items 1) to 3) above, wherein said porous pigment is a silica pigment.

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5) The recording medium according to any one of items 1) to 4) above, which is used for ink jet recording.

6) An aqueous ink composition comprising a colorant, water, and 0.01 to 2% by weight of at least one benzotriazole compound represented by formula (I):

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wherein R represents a hydrogen atom or an alkyl group; X represents a hydrogen atom, a sodium atom, a potassium atom or a primary, secondary or tertiary amino group.

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7) The aqueous ink composition according to item 6) above, wherein said benzotriazole compound comprises at least one of benzotriazole, benzotriazole sodium salt, 4-methylbenzotriazole, 4-methylbenzotriazole sodium salt, and a benzotriazole amine salt.

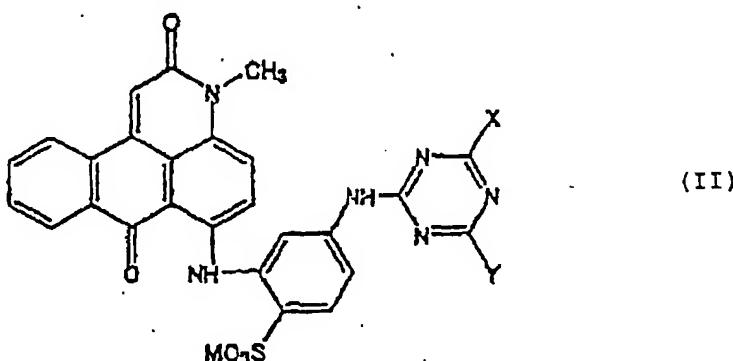
8) The aqueous ink composition according to item 6) or 7) above, wherein said colorant is a dye.

9) The aqueous ink composition according to item 8) above, wherein said dye is represented by formula (II):

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wherein X represents anilino group substituted by at least one SO_3M group, Y represents OH, Cl or a morpholino group, and M represents a member selected from H, Li, Na, K, ammonium and organic amines.

10) The aqueous ink composition according to any one of items 6) to 9) above, which is used for ink jet recording.

11) The aqueous ink composition according to any one of items 6) to 10) above, which is used for forming an image on a recording medium having an ink receiving layer comprising a porous pigment and a binder.

5 12) An ink jet recording method comprising forming an image on a recording medium according to any one of items 1) to 5) above with an aqueous ink composition containing a dye represented by formula (II):

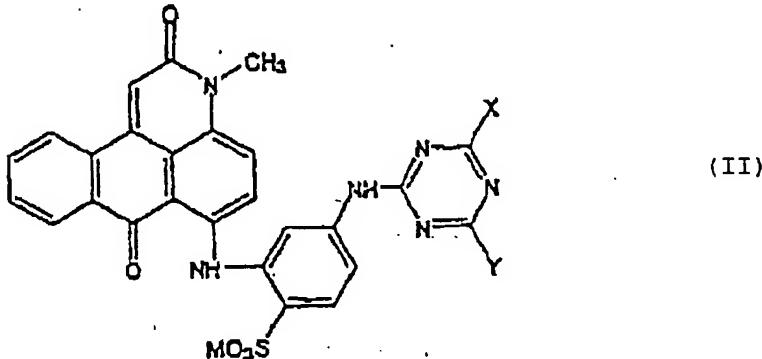
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wherein X represents anilino group substituted by at least one SO_3M group, Y represents OH, Cl or a morpholino group, and M represents a member selected from H, Li, Na, K, ammonium and organic amines.

13) An ink jet recording method comprising ejecting a droplet of an aqueous ink composition according to any one of items 6) to 11) above to attach the ejected droplet onto a recording medium, thereby performing printing.

DETAILED DESCRIPTION OF THE INVENTION

[0011] The recording medium according to the present invention is classified into a void type in which the ink receiving layer comprises a porous pigment and a binder. The ink receiving layer further comprises a benzotriazole compound of formula (I).

[0012] In formula (I), R represents a hydrogen atom or an alkyl group. The alkyl group includes a substituted or unsubstituted methyl group and a substituted or unsubstituted ethyl group. R is preferably a hydrogen atom.

[0013] X represents a hydrogen atom, a sodium atom, a potassium atom or a primary, secondary or tertiary amino group. The primary amino group includes methylamino, ethylamino and propylamino. The secondary amino group includes dimethylamino, diethylamino, and N-methylethylamino. The tertiary amino group includes trimethylamino, triethylamino, N,N-dimethylethylamino, and N,N-diethylmethylamino. X is preferably a hydrogen atom.

[0014] Preferred examples of the benzotriazole compounds represented by formula (I) are benzotriazole, benzotriazole sodium salt, 4-methylbenzotriazole, 4-methylbenzotriazole sodium salt, and a benzotriazole amine salt. Benzotriazole is particularly preferred for its solubility. These benzotriazole compounds can be used either individually or as a combination of two or more thereof.

[0015] The amount of the benzotriazole compound of formula (I) in the ink receiving layer is preferably 0.01 to 5% by weight, still preferably 0.1 to 3% by weight. With a benzotriazole compound content less than 0.01% by weight, the improving effects on light fastness and gas fastness tend to be insubstantial, failing to sufficiently protect the colorant against air-mediated deterioration. When added in amounts exceeding 5% by weight, the benzotriazole compound tends to impair ink absorptivity of the ink receiving layer.

[0016] The porous pigment which can be used in the ink receiving layer includes silica pigments (e.g., silica prepared by a precipitation method or a gas phase method and silica gel), smectite, calcium carbonate, calcium sulfate, barium sulfate, titanium dioxide, kaolin, white clay, talc, magnesium silicate, and calcium silicate. They can be used either individually or as a mixture thereof. Preferred of them are silica pigments for their high purity, competitive price and availability. Particularly preferred are silica by a precipitation method and silica gel.

[0017] It is preferred for the porous pigment to have a BET specific surface area of 100 to 500 m^2/g , particularly 200 to 400 m^2/g , from the standpoint of balance between image quality (e.g., color developability and resolving power) and image preservability. Where the BET specific surface area is less than 100 m^2/g , the image density tends to be reduced.

If it is more than 500 m²/g, there is a fear that the colorant cannot be sufficiently prevented from air-mediated deterioration, and the recorded image may have poor preservability.

[0018] The average particle size of the porous pigment is selected from the range generally usable as a pigment. From the viewpoint of smoothness of the ink receiving layer and for improvement on image quality such as resolving power, a preferred average particle size is 0.05 to 15 µm, particularly 0.1 to 10 µm.

[0019] The content of the porous pigment in the ink receiving layer preferably ranges from 40 to 90% by weight, particularly 50 to 80% by weight. With a porous pigment content less than 40% by weight, ink absorptivity may be insufficient. With a porous pigment content more than 90% by weight, the ink receiving layer tends to have reduced film strength.

[0020] The binder which can be used to make the ink receiving layer is not particularly limited and includes any substance capable of binding the porous pigment particles and increasing the film strength. Suitable binders include polyvinyl alcohol, silanol-modified polyvinyl alcohol, polyvinyl acetate, starch, cellulose derivatives (e.g., carboxymethyl cellulose), casein, gelatin, latices of conjugated diene copolymers (e.g., a styrene-butadiene copolymer), latices of vinyl copolymers (e.g., an ethylene-vinyl acetate copolymer), and latices of acrylic copolymers (e.g., copolymers of acrylic acid or methacrylic acid). These binders can be used either individually or as a mixture thereof. Of the above-recited binders particularly preferred is polyvinyl alcohol.

[0021] The binder is preferably used in a proportion of 5 to 60%, particularly 10 to 50% by weight, based on the porous pigment. With a binder proportion less than 5% by weight, the ink receiving layer tends to have reduced strength. In proportions exceeding 60% by weight, ink absorptivity or colorant adsorptivity tends to be reduced.

[0022] If desired, the ink receiving layer can contain one or more additives, such as dye fixatives, fluorescent whitening agents, waterproofing agents, antifungal agents, preservatives, dispersants, surface active agents, thickeners, pH adjustors, defoaming agents, and humectants.

[0023] The dye fixatives include cationic organic substances, polyvalent metal ions, and cationic surface active agents.

[0024] The cationic organic substances include low molecular compounds, such as primary, secondary or tertiary amines, primary, secondary or tertiary amine salts, and quaternary ammonium salts; and oligomers or polymers having a primary, secondary or tertiary amino group, a primary, secondary or tertiary amine base, or a quaternary ammonium base. Specific examples are a diallyldimethylammonium chloride polymer, an epihalohydrin-secondary amine copolymer, a diallyldimethylammonium chloride-sulfur dioxide copolymer, a diallyldimethylammonium chloride-acrylamide copolymer, a diallylmethylammonium salt polymer, a diallylamine hydrochloride-sulfur dioxide copolymer, a dimethyl-methylamine hydrochloride copolymer, polyallylamine, polyethyleneimine, polyethyleneimine quaternary ammonium salt, a (meth)acrylamidoalkylammonium salt polymer, and ionene having a quaternary ammonium base. The polyvalent metal ions include Al³⁺, Ca²⁺, and Mg²⁺. The cationic surface active agents include benzalkonium chloride. These dye fixatives can be used either individually or as a combination of two or more thereof. Polymers having a quaternary ammonium base are particularly preferred as a dye fixative.

[0025] The dye fixative is preferably used in an amount of 0.5 to 15% by weight, particularly 1 to 10% by weight, based on the ink receiving layer. Amounts less than 0.5% by weight are ineffective in improving color developability and water resistance of a recorded image. When added in amounts exceeding 15% by weight, the dye fixative tends to reduce ink absorptivity or induce the colorant to bleed to cause bronzing.

[0026] The substrate on which the ink receiving layer is provided includes paper (including sized paper), resin-coated (e.g., paper coated with polyethylene, polypropylene or polyester), photographically useful substrates such as baryta paper and so-called RC paper, thermoplastic resin films of polyethylene terephthalate, polyethylene, polypropylene, etc., synthetic paper, and sheeting formed of synthetic fiber.

[0027] The substrate preferably has a basis weight of 50 to 120 g/m², particularly 70 to 100 g/m², and a thickness of 100 to 240 µm, particularly 140 to 200 µm.

[0028] The recording medium of the invention is typically produced by coating the substrate with an aqueous coating composition prepared from the benzotriazole compound of formula (I), the porous pigment, the binder, and necessary additives (e.g., dye fixatives) by any known coating technique, such as roll coating, blade coating, air knife coating, gate roll coating or size pressing, and drying the coating layer by a known means, such as a hot air drier or a far-infrared drier. In order to improve the surface strength and smoothness of the ink receiving layer, the coating layer thus provided can be calendered to an extent that does not impair the ink absorptivity.

[0029] The coating weight of the ink receiving layer is preferably 10 to 40 g/m², still preferably 20 to 30 g/m², on a solid basis. Where it is less than 10 g/m², the effect in improving color developability of dyes is insubstantial. A coating weight more than 40 g/m² is liable to cause dusting. The thickness of the ink receiving layer is preferably 10 to 40 µm, still preferably 20 to 30 µm.

[0030] The ink receiving layer preferably has a void of 30 to 80%, particularly 40 to 70%. The ink receiving layer which has a void less than 30% tends to be unsatisfactory in ink drying properties, absorption rate, absorption capacity, and the like. If the void is more than 80%, the porous pigment is apt to fall off to cause slippage of a paper feed roll or

clogging of a recording head. The void of the ink receiving layer can be adjusted within the above range by calendering and the like. The void of the ink receiving layer is measured in accordance with J. TAPPI No. 48-85.

[0031] The recording medium of the invention can be recorded with any ink commonly used in ink jet recording or the like recording systems. Such ink is generally aqueous ink comprising a colorant, such as a dye or a pigment, and water. The colorant of the aqueous ink being prevented from air-mediated deterioration by the action of the benzotriazole compound of formula (I) in the ink receiving layer, the image formed on the recording medium of the invention with the aqueous ink is excellent in light fastness and gas fastness and can be stored indoors for a long period of time with little discoloration. In particular, an image formed on the recording medium of the invention with aqueous ink containing a magenta dye represented by formula (II) (hereinafter described) is particularly superior in light fastness.

10 Being of void type, the recording medium of the invention exhibits excellent ink absorbing properties (quick drying properties) even where recording is carried out with an increased ink output.

[0032] The aqueous ink composition according to the present invention comprises at least a colorant, water, and 0.01 to 2% by weight, preferably 0.1 to 1% by weight, of at least one benzotriazole compound of formula (I). If the content of the benzotriazole compound is less than 0.01% by weight, no improving effects on light fastness and gas 15 fastness is produced. If it is more than 2% by weight, the flying properties of ink droplets may change, and nozzles tend to be clogged.

[0033] The colorant which can be used in the aqueous ink composition includes dyes and pigments. Dyes are preferred to pigments for high color density developed per unit weight and brightness of colors. Water-soluble dyes are still preferred, such as acid dyes, direct dyes, mordant dyes, reactive dyes, solubilized vat dyes, solubilized sulfur dyes, 20 food colors, etc. as classified in Color Index.

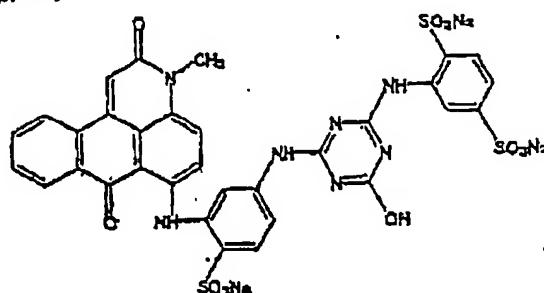
[0034] The effects of the present invention in providing an image excellent in gas fastness and light fastness are pronounced particularly where dyes having poor light fastness and gas fastness are used.

[0035] While the aqueous ink composition containing the benzotriazole compound of formula (I) provides a light-fast 25 image by itself, a more light-fast image can be obtained where the aqueous ink composition contains a magenta dye represented by formula (II).

[0036] Examples of preferred dyes of formula (II) include dyes M-1 to M-10 shown below. They can be used either individually or as a combination thereof.

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M - 1

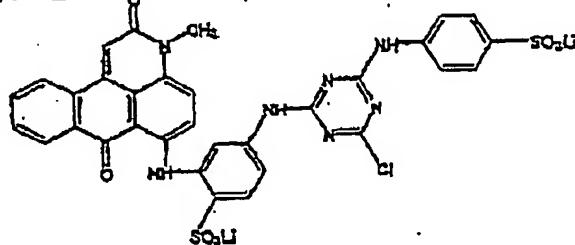


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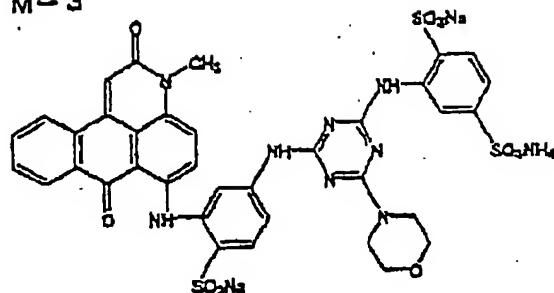
M - 2



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M - 3



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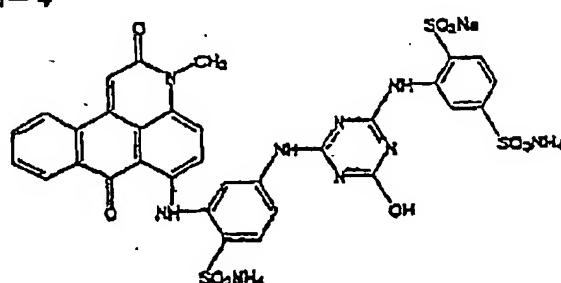
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M - 4

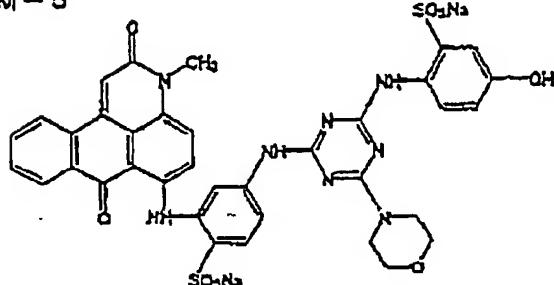


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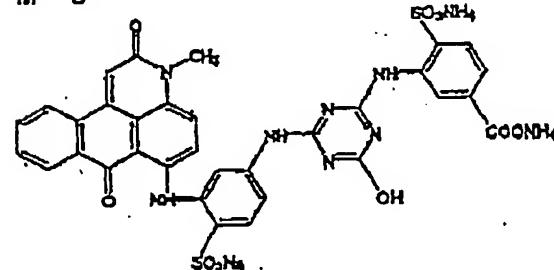
M - 5



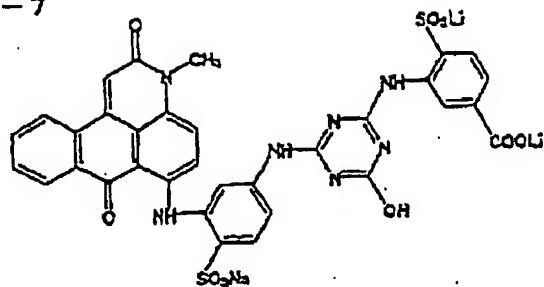
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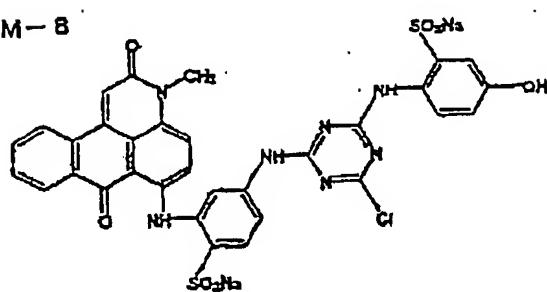
M - 6



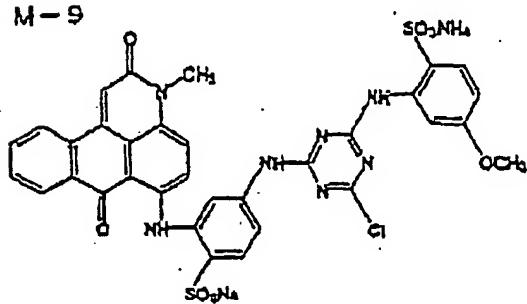
M-7



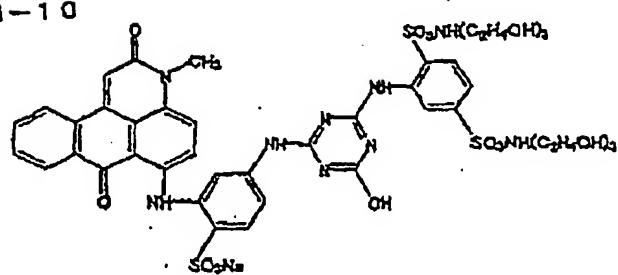
M-8



M-9



M-10



[0037] Water which is used as a main solvent of the aqueous ink composition includes pure water or ultrapure water, such as ion-exchanged water, ultrafiltered water, reverse osmotic water, and distilled water. Water sterilized by UV irradiation or addition of hydrogen peroxide is advantageous for antifungal or antibacterial control.

5 [0038] If desired, the aqueous ink composition can contain one or more additives, such as penetrants, surface active agents, wetting agents, anti-clogging agents, preservatives or antifungals, pH adjustors, dissolution aids, antioxidants, surface tension modifiers, viscosity modifiers, dielectric constant modifiers, oxygen absorbers, and so forth.

10 [0039] Recording media suitable for recording with the aqueous ink composition of the invention are those of void type in which the ink receiving layer comprises a porous pigment and a binder. Images recorded on void type recording media with the aqueous ink composition of the invention exhibit excellent fastness to light and gas and withstand long-term preservation.

15 [0040] The recording medium and the aqueous ink composition according to the present invention are suited chiefly to ink jet recording. Any ink jet recording system in which ink droplets are ejected and fixed to a recording medium is applicable. Particularly suitable is drop-on-demand ink jet recording, which includes a piezoelectric system using a piezoelectric element disposed on a printer head and a thermal jet system utilizing heat energy of a resistance heating element disposed on a printer head. The recording medium and the aqueous ink composition of the invention manifest excellent effects in any of these recording methods.

20 [0041] Various changes and modifications can be made in the present invention without departing from the spirit thereof. For example, the ink receiving layer can be provided on either one or both sides of the substrate. The recording medium can be produced by coating a substrate with a coating composition comprising the above-described components except the benzotriazole compound and, after drying the coating layer, applying an aqueous solution of the benzotriazole compound to the coated layer by dipping, size pressing, spraying or a like method.

25 [0042] The aqueous ink composition of the invention is not particularly restricted, except that it contains a specific amount of the benzotriazole compound of formula (I), and formulations and ingredients generally employed in recording ink of this type can be used.

[0043] The present invention will now be illustrated in greater detail with reference to Examples, but the invention should not be construed as being limited thereto. Unless otherwise noted, all the parts and percents are by weight.

EXAMPLE 1

30 [0044] A coating composition having the following formulation was applied to a substrate (Lumirror 125T, available from Toray Ind., Inc.) to a dry coating weight of 20 g/m² by means of an air knife coater and dried in a hot air drier at 140°C for 3 minutes to prepare a recording medium (designated recording medium 1):

Formulation of coating composition:		
35 Silica (Fine Seal X37B, available from Tokuyama Corp.)		100 parts
Polyvinyl alcohol (10% aqueous solution; Gohsenal T-330, available from The Nippon Synthetic Chemical Ind. Co., Ltd.)		400 parts
40 Cationic polymer (Neofix RP-70, available from Nikka Kagaku Kogyo K.K.)		25 parts
Benzotriazole		3 parts
45 Water		600 parts

EXAMPLE 2

50 [0045] A recording medium 2 was prepared in the same manner as in Example 1, except for replacing benzotriazole with 3 parts of 4-methylbenzotriazole.

EXAMPLE 3

55 [0046] Ink components shown below were mixed and filtered under pressure through a membrane filter having a pore size of 1 µm to prepare a set of color inks (cyan, magenta, and yellow) designated ink set 1.

Formulation of cyan (C) ink:		
5	C.I. Direct Blue 199	3.0 parts
10	Benzotriazole	1.0 part
15	Triethylene glycol monobutyl ether	10 parts
20	Diethylene glycol	10 parts
25	Glycerol	10 parts
30	Triethanolamine	1.0 part
35	Disodium ethylenediaminetetraacetate	0.01 part
40	Olfin E1010 (acetylene glycol surface active agent available from Nissin Chemical Ind. Co., Ltd.)	1.0 part
45	Proxel XL-2	0.3 part
50	Ion-exchanged water	65 parts

Formulation of magenta (M) ink:		
30	C.I. Acid Red 52	1.5 parts
35	C.I. Acid Red 240	1.5 parts
40	Benzotriazole	1.0 part
45	Triethylene glycol monobutyl ether	10 parts
50	Diethylene glycol	10 parts
	Glycerol	10 parts
	Triethanolamine	1.0 part
	Disodium ethylenediaminetetraacetate	0.01 part
	Olfin E1010	1.0 part
	Proxel XL-2	0.3 part
	Ion-exchanged water	65 parts

Formulation of yellow (Y) ink:		
55	C.I. Acid Yellow 32	2.0 parts
	Benzotriazole	1.0 part

(continued)

Formulation of yellow (Y) ink:		
5	Triethylene glycol monobutyl ether	10 parts
10	Diethylene glycol	10 parts
15	Glycerol	10 parts
20	Triethanolamine	1.0 part
	Disodium ethylenediaminetetraacetate	0.01 part
	Olfin E1010	1.0 part
	Proxel XL-2	0.3 part
	Ion-exchanged water	65 parts

EXAMPLE 4

25 [0047] A set of C, M and Y color inks (designated ink set 2) were prepared in the same manner as in Example 3, except for using 4-methylbenzotriazole in place of benzotriazole in the same concentration.

EXAMPLE 5

30 [0048] A set of C, M and Y inks (designated ink set 3) were prepared in the same manner as in Example 3, except that the M ink had the following formulation.

Formulation of magenta ink (M):		
35	Dye M-1	4 parts
40	Benzotriazole	1 part
45	Triethylene glycol monobutyl ether	10 parts
50	Diethylene glycol	10 parts
55	Glycerol	10 parts
	Triethanolamine	1 part
	Disodium ethylenediaminetetraacetate	0.01 part
	Olfin E1010	1 part
	Proxel XL-2	0.3 part
	Ion-exchanged water	65 parts

COMPARATIVE EXAMPLE 1

[0049] A recording medium (designated recording medium 3) was prepared in the same manner as in Example 1, except that benzotriazole was not used in the coating composition.

[0050] Ink set 4 was prepared in the same manner as in Example 3, except that benzotriazole was not used.

COMPARATIVE EXAMPLE 2

[0051] Ink set 5 was prepared in the same manner as in Example 5, except that benzotriazole was not used.

COMPARATIVE EXAMPLE 3

[0052] Recording medium 4 was prepared in the same manner as in Example 1, except for using a coating composition having the following formulation.

Formulation of coating composition:	
Silica (Fine Seal X37B)	100 parts
Polyvinyl alcohol (10% aqueous solution; Gohsenal T-330)	400 parts
Cationic polymer (Neofix RP-70)	25 parts
Benzotriazole UV absorber (solid content: 30%; AdekaStab LX-301 available from Asahi Denka Kogyo K.K.)	10 parts
Water	600 parts

COMPARATIVE EXAMPLE 4

[0053] Recording medium 5 was prepared in the same manner as in Example 1, except that a coating composition having the following formulation was applied to a dry coating weight of 10 g/m².

Formulation of coating composition:	
Lime-processed gelatin	70 parts
Polyvinylpyrrolidone (PVP-90, available from BASF)	70 parts
Cationic polymer (Neofix RP-70)	25 parts
Benzotriazole	3 parts
Surface active agent (Megafax F-120, available from Dainippon Ink & Chemicals Inc.)	1 part
Water	1800 parts

Evaluation of Light Fastness, Indoor Preservability, Ozone Fastness, and Ink Absorptivity:

[0054] Recording media 1 to 5 were printed solid in each of C, M, Y, and a composite black (Bk) according to the combination shown in Table 1 below on an ink jet printer MJ-030C supplied by Seiko Epson Corp. The monochromatic solid images were evaluated according to the following methods. The results obtained are shown in Table 1 below. The printing method was arranged so that the composite black is composed of three aqueous recording inks of C, M and Y.

1) Light fastness:

[0055] The C, M or Y image was subjected to 50-hour accelerated exposure testing in a Ci35A Weatherometer from Atlas Electric Device Co. under conditions of a temperature of 40°C, a relative humidity of 50%, a black panel temperature of 63°C, and an irradiance of 0.25 W/m² measured at 340 nm. Color fading was expressed as a retention (%) of optical density (ROD) as measured with a Gretag densitometer. A greater ROD indicates higher light fastness.

$$ROD (\%) = (D/D_1) \times 100$$

10 D: OD after exposure; D₁: OD before exposure

2) Indoor preservability:

15 [0056] The image printed in Bk was left to stand as stuck on the wall of a room kept at 24°C and 60% RH for 1 month, and a color difference (ΔE^{*ab}) of the Bk image from the color immediately after printing was obtained according to JIS Z8730. A smaller ΔE^{*ab} indicates higher indoor preservability.

20 3) Ozone fastness:

[0057] The image printed in Bk was left to stand in a light-shielded container having an ozone concentration of 10 ppm at 24°C and 60% RH for 120 minutes. A color difference (Δ^{*Eab}) of the Bk image from the color before ozone treatment was obtained according to JIS Z8730. A smaller Δ^{*Eab} means higher ozone fastness.

25 4) Ink absorptivity:

[0058] Monochromatic C, M and Y images were printed on the ink jet printer MJ-030C on recording media 1 to 5 according to the combination shown in Table 1 to give a reflective density of 2.0 or more in each color. Immediately after printing, paper for a plain paper copier was superposed on the printed area and pressed lightly. The amount of the ink transferred to the paper was observed with the naked eye and rated as follows.

30 Standard for rating:

- 35 A ... No transfer
- B ... Slight transfer
- C ... Considerable transfer

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Combination No.	Recording Medium	Ink Set	Light Fastness (ROD, %)			Indoor Preservability' ($\Delta E'_{ab}$)	Ozone Fastness' ($\Delta E'_{ab}$)	Ink Absorptivity	Remark
			Y	M	C				
1	1	4	80	75	98	1.2	8.0	A	Invention
2	2	4	78	74	97	1.3	8.2	A	*
3	3	1	82	76	97	1.2	8.1	A	*
4	3	2	81	76	98	1.2	8.1	A	*
5	3	3	82	82	97	1.2	8.0	A	*
6	1	5	80	81	98	1.3	8.1	A	*
7	3	4	68	62	92	3.6	12.3	A	Comparison
8	3	5	68	63	92	3.7	12.5	A	*
9	4	4	76	59	96	1.8	9.2	A	*
10	5	4	75	65	90	1.1	7.2	C	*

Note: * Measured on the Bk image.

[0059] As is apparent from the results in Table 1, recorded images formed on recording medium 1 or 2 containing the benzotriazole compound of formula (I) (combination Nos. 1, 2 and 6) and the images formed with ink sets 1, 2 or 3 containing the benzotriazole compound of formula (I) (combination Nos. 3 to 5) are superior in light fastness, indoor preservability and ozone fastness to those formed on recording medium 3, 4 or 5 with ink set 4 or 5, neither of which contains the benzotriazole compound of formula (I) (combination Nos. 7 to 10). The image of combination No. 9, in which recording medium 4 contains a commonly employed benzotriazole UV absorber, is inferior to the images of the combinations according to the present invention in all these characteristics, clearly proving the effectiveness of the benzotriazole compound of formula (I). To make it worse, the ink receiving layer of recording medium 4 is tinged with yellow and practically useless.

[0060] It is also seen that the magenta images of combination Nos. 5 and 6, in which magenta dye (M-1) is used in the magenta ink composition, exhibit higher light fastness than the other magenta images.

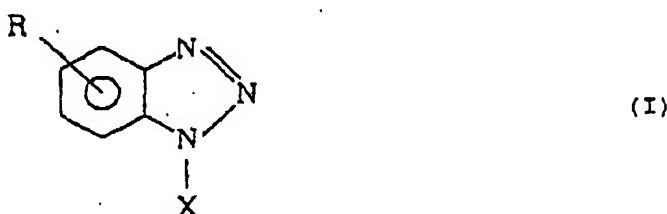
[0061] The image of combination No. 10 formed on recording medium 5, which is of swell type, has poor ink absorptivity compared with those of other combinations.

5 [0062] The recording medium, the aqueous ink composition, and the ink jet recording method according to the present invention provide an image excellent in light fastness and gas fastness, particularly an image that can be preserved indoors for a long period of time with little color change and fading with time. The recording medium and the aqueous ink composition according to the present invention are suitable for use in ink jet recording. The recording medium of the invention, being of void type, is fit for high-quality image formation with an increased ink output.

10 [0063] While the present invention has been described in detail with reference to specific examples thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

15 1. A recording medium having an ink receiving layer comprising a porous pigment and a binder, wherein said ink receiving layer contains at least one benzotriazole compound represented by formula (I):



wherein R represents a hydrogen atom or an alkyl group; X represents a hydrogen atom, a sodium atom, a potassium atom or a primary, secondary or tertiary amino group.

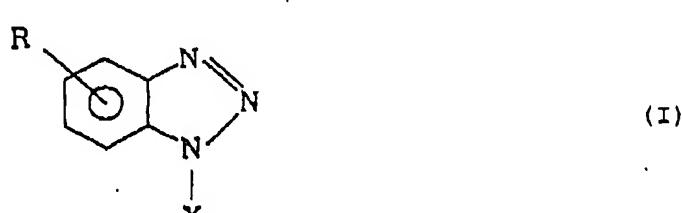
30 2. The recording medium according to claim 1, wherein said benzotriazole compound comprises at least one of benzotriazole, benzotriazole sodium salt, 4-methylbenzotriazole, 4-methylbenzotriazole sodium salt, and a benzotriazole amine salt.

35 3. The recording medium according to claim 1 or 2, wherein said benzotriazole compound is present in a total amount of 0.01 to 5% by weight based on the weight of said ink receiving layer.

40 4. The recording medium according to any one of claims 1 to 3, wherein said porous pigment is a silica pigment.

45 5. The recording medium according to any one of claims 1 to 4, which is used for ink jet recording.

50 6. An aqueous ink composition comprising a colorant, water, and 0.01 to 2% by weight of at least one benzotriazole compound represented by formula (I):



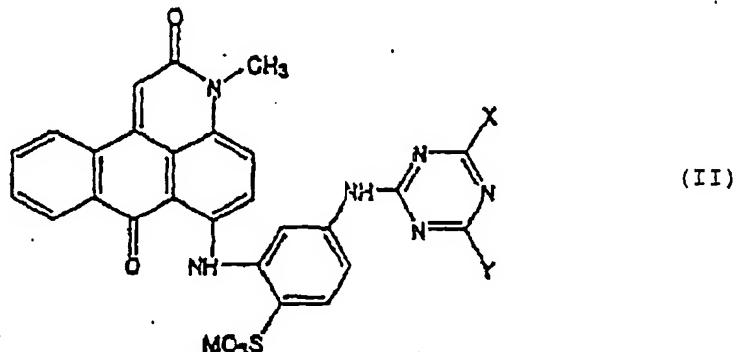
55 wherein R represents a hydrogen atom or an alkyl group; X represents a hydrogen atom, a sodium atom, a potassium atom or a primary, secondary or tertiary amino group.

7. The aqueous ink composition according to claim 6, wherein said benzotriazole compound comprises at least one

of benzotriazole, benzotriazole sodium salt, 4-methylbenzotriazole, 4-methylbenzotriazole sodium salt, and a benzotriazole amine salt.

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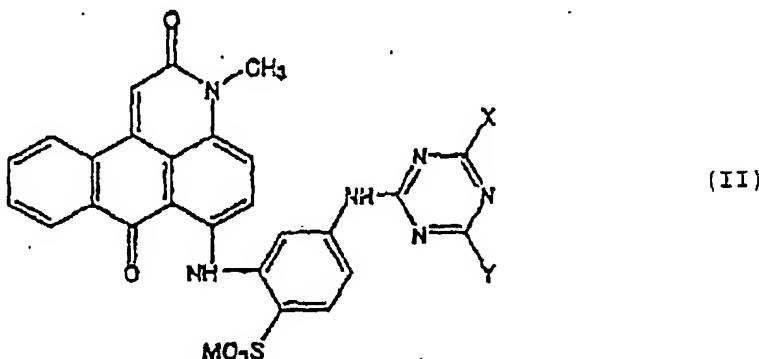
8. The aqueous ink composition according to claim 6 or 7, wherein said colorant is a dye.
9. The aqueous ink composition according to claim 8, wherein said dye is represented by formula (II):



wherein X represents anilino group substituted by at least one SO_3M group, Y represents OH, Cl or a morpholino group, and M represents a member selected from H, Li, Na, K, ammonium and organic amines.

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10. The aqueous ink composition according to any one of claims 6 to 9, which is used for ink jet recording.
11. The aqueous ink composition according to any one of claims 6 to 10, which is used for forming an image on a recording medium having an ink receiving layer comprising a porous pigment and a binder.
12. An ink jet recording method comprising forming an image on a recording medium according to any one of claims 1 to 5 with an aqueous ink composition containing a dye represented by formula (II):



wherein X represents anilino group substituted by at least one SO_3M group, Y represents OH, Cl or a morpholino group, and M represents a member selected from H, Li, Na, K, ammonium and organic amines.

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13. An ink jet recording method comprising ejecting a droplet of an aqueous ink composition according to any one of claims 6 to 11 to attach the ejected droplet onto a recording medium, thereby performing printing.



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EUROPEAN SEARCH REPORT

Application Number

EP 01 11 2463

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	JP 11 302587 A (SAKURA KUREPASU) 2 November 1999 (1999-11-02)	6-8,10, 13	B41M5/00 C09D11/00
Y	* page 3, right-hand column, paragraph 24 * * page 4, left-hand column, paragraphs 30,31 * * page 6, left-hand column, paragraph 56 * * page 7; table 1 *	9	
X	EP 0 978 547 A (SEIKO EPSON) 9 February 2000 (2000-02-09)	6-8,10, 13	
Y	* page 10, line 24 - line 27 *	9	
X	EP 0 959 112 A (SEIKO EPSON) 24 November 1999 (1999-11-24)	6-8,10, 13	
Y	* page 5, line 22 - line 23; claims 1,3 *	9	
X	EP 0 878 522 A (SEIKO EPSON) 18 November 1998 (1998-11-18)	6-8,10, 13	
Y	* page 4, line 1 - line 2 * * page 10, line 28 - line 29 *	9	
X	EP 0 803 554 A (DAINICHISEIKA COLOR & CHEMICALS) 29 October 1997 (1997-10-29)	6-8,10, 13	B41M C09D
Y	* page 2, line 16 - line 25 * * page 7, line 1 - line 5 *	9	
X	EP 0 761 783 A (SEIKO EPSON) 12 March 1997 (1997-03-12)	6-8,10, 13	
Y	* page 5, line 34 - line 36 * * page 15, line 18 - line 19 *	9	
X	EP 0 651 037 A (SEIKO EPSON) 3 May 1995 (1995-05-03)	6-8,10, 13	
Y	* claims 4,8,9 *	9	
		-/-	
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	17 September 2001	Magrizos, S	
CATEGORY OF CITED DOCUMENTS			
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Application Number
EP 01 11 2463

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	WO 00 22056 A (SEIKO EPSON) 20 April 2000 (2000-04-20)	6-8,10, 13	
Y	* page 23, line 16 - line 20; claims 1,15 * ---	9	
X	WO 98 30642 A (FORMULABS) 16 July 1998 (1998-07-16)	6-8,10, 13	
Y	* page 13, line 10 - line 29 *	9	
X	US 5 614 008 A (ESCANO ET AL.) 25 March 1997 (1997-03-25)	6-8,10, 13	
Y	* column 1, line 6 - line 10 * * column 13, line 5 - line 16 * * column 16, line 54 - line 55 *	9	
X	EP 0 514 633 A (FELIX SCHÖLLER) 25 November 1992 (1992-11-25)	1-3,5	
Y	* page 2, line 1 * * page 3, line 19 - line 25; claims 9,15 *	4,11,12	
X	US 5 858 514 A (BOWERS) 12 January 1999 (1999-01-12) * column 2, line 46 - line 50 * * column 7, line 64 - column 8, line 18; claim 1 *	1,2,5	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
Y	WO 00 23440 A (NIPPON KAYAKU) 27 April 2000 (2000-04-27) * page 1, line 22 - page 2, line 4 * * page 11; table 1 * * claims 1,2,13 *	4,9,11, 12	
Y	WO 99 48981 A (NIPPON KAYAKU) 30 September 1999 (1999-09-30) * page 1, line 23 - page 2, line 4; claims 1,2,10 *	4,9,11, 12	
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	17 September 2001	Magrizos, S	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone	T : theory or principle underlying the invention		
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EP 01 11 2463

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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17-09-2001

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
JP 11302587	A	02-11-1999	US	6171381 B1	09-01-2001
EP 978547	A	09-02-2000	EP	0978547 A1	09-02-2000
			JP	2000327974 A	28-11-2000
EP 959112	A	24-11-1999	EP	0959112 A1	24-11-1999
			JP	2001001627 A	09-01-2001
EP 878522	A	18-11-1998	EP	0878522 A1	18-11-1998
			JP	11080639 A	26-03-1999
			US	6051057 A	18-04-2000
EP 803554	A	29-10-1997	AU	724924 B2	05-10-2000
			AU	1900997 A	30-10-1997
			CA	2203205 A1	22-10-1997
			CN	1165163 A	19-11-1997
			DE	69705888 D1	06-09-2001
			EP	0803554 A2	29-10-1997
			JP	10046070 A	17-02-1998
			US	5913972 A	22-06-1999
EP 761783	A	12-03-1997	EP	0761783 A2	12-03-1997
			JP	10095941 A	14-04-1998
			US	6004389 A	21-12-1999
			US	5746818 A	05-05-1998
EP 651037	A	03-05-1995	EP	0651037 A1	03-05-1995
			JP	3089665 B2	18-09-2000
			US	5560771 A	01-10-1996
			EP	1004643 A2	31-05-2000
			WO	9426828 A1	24-11-1994
			JP	2000154344 A	06-06-2000
			SG	46629 A1	20-02-1998
WO 0022056	A	20-04-2000	EP	1041127 A1	04-10-2000
			WO	0022056 A1	20-04-2000
WO 9830642	A	16-07-1998	US	5897694 A	27-04-1999
			AU	5623198 A	03-08-1998
			EP	0951516 A1	27-10-1999
			JP	2001508482 T	26-06-2001
			WO	9830642 A1	16-07-1998
US 5614008	A	25-03-1997	AT	183767 T	15-09-1999
			AU	7449896 A	15-05-1997
			BR	9611165 A	30-03-1999

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 01 11 2463

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

17-09-2001

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5614008	A		DE 69603972 D1 DE 69603972 T2 EP 0857197 A1 JP 11513743 T WO 9715634 A1 US 5665151 A ZA 9608872 A	30-09-1999 05-01-2000 12-08-1998 24-11-1999 01-05-1997 09-09-1997 28-05-1997
EP 514633	A	25-11-1992	DE 4116595 A1 AT 139946 T DE 59206685 D1 DK 514633 T3 EP 0514633 A1 ES 2089264 T3 GR 3020769 T3 JP 5131741 A	26-11-1992 15-07-1996 08-08-1996 18-11-1996 25-11-1992 01-10-1996 30-11-1996 28-05-1993
US 5858514	A	12-01-1999	NONE	
WO 0023440	A	27-04-2000	EP 1123932 A1 WO 0023440 A1 JP 2000191660 A	16-08-2001 27-04-2000 11-07-2000
WO 9948981	A	30-09-1999	CN 1295600 T EP 1067155 A1 JP 2000109464 A WO 9948981 A1	16-05-2001 10-01-2001 18-04-2000 30-09-1999